



CERTIFICATE OF VERIFICATION

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hereby state that I am the translator of the attached document and certify that the attached document is an accurate translation to the best of my knowledge of the certified copy of Japanese Patent Application No. 2001-032697 filed February 8, 2001.

Signed this 6th day of July, 2006

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Date of Application: February 8, 2001

Application Number: Patent Application No. 2001-032697

Applicant(s): Showa Denko Kabushiki Kaisha

December 14, 2001

Commissioner,
Japan Patent Office Kozo Oikawa (Seal)

Issuance No. 2001-3108884

[Name of Document]	Patent Application
[Reference Number]	PSDK0232
[Filing Date]	February 8, 2001
[Address]	Commissioner, Patent Office
[Intl. Patent Cl.]	H01B17/50 H01C 1/08 D01F 9/127
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[Indication of Fee]	
[Deposit Ledger Number]	054634
[Paid Amount]	21,000 yen

[List of Submitted Articles]

[Name of Article]	Specification	1
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[Name of Article]	Abstract	1
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[Comprehensive Power of

Attorney Number]	9722913
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[Necessity of Proof]	Necessary
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[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

Electrical Insulating Vapor Grown Carbon Fiber and
Method for Producing the Same, and Use Thereof

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] An electrical insulating vapor grown carbon fiber comprising a vapor grown carbon fiber having a fiber diameter of 0.01 to 0.5 μm with a part or the whole of the surface thereof being coated with an electrical insulating material.

[Claim 2] The electrical insulating vapor grown carbon fiber as claimed in claim 1, wherein the electrical insulating material is boron nitride,

[Claim 3] The electrical insulating vapor grown carbon fiber as claimed in claim 2, wherein the boron nitride content is 2% by mass or more based on the entire amount of vapor grown carbon fiber and the Co value is 0.680 nm or less.

[Claim 4] The electrical insulating vapor grown carbon fiber as claimed in claim 2 or 3, wherein the boron content in the depth of 1 nm from the surface of vapor grown carbon fiber is 10% by mass or more.

[Claim 5] The electrical insulating vapor grown carbon fiber as claimed in any one of claims 1 to 4, wherein when compressed to a bulk density of 0.8 g/cm^3 , the

resistivity is $10^3 \Omega \cdot \text{cm}$ or more and the heat conductivity is $150 \text{ Wm}^{-1}\text{K}^{-1}$ or more.

[Claim 6] A method for producing an electrical insulating vapor grown carbon fiber, comprising mixing a boron compound with a vapor grown carbon fiber having a fiber diameter of 0.01 to 0.5 μm , and heat-treating the mixture at $2,000^\circ\text{C}$ or more in the presence of a nitrogen compound.

[Claim 7] A method for producing an electrical insulating vapor grown carbon fiber coated with boron nitride, comprising mixing a boron compound with a vapor grown carbon fiber having a fiber diameter of 0.01 to 0.5 μm , compressing said mixture and heat-treating the compressed mixture at $2,000^\circ\text{C}$ or more in the presence of a nitrogen compound.

[Claim 8] The method for producing an electrical insulating vapor grown carbon fiber as claimed in claim 6 or 7, wherein the nitrogen compound is nitrogen.

[Claim 9] The method for producing an electrical insulating vapor grown carbon fiber as claimed in any one of claims 6 to 8, wherein the boron compound is at least one member selected from the group consisting of elementary boron, boric acid, borate, boron oxide, B_4C and boron nitride.

[Claim 10] The method for producing an electrical

insulating vapor grown carbon fiber as claimed in any one of claims 6 to 9, wherein the mixture of a boron compound and a vapor grown carbon fiber has a boron concentration of 1 to 30% by mass in terms of boron element.

[Claim 11] An electrical insulating composite material comprising a synthetic resin or synthetic rubber composition containing an electrical insulating vapor grown carbon fiber comprising a vapor grown carbon fiber having a fiber diameter of 0.01 to 0.5 μm with a part or the whole of the surface being coated with an electrical insulating material.

[Claim 12] The electrical insulating composite material as claimed in claim 11, wherein the electrical insulating material is boron nitride.

[Claim 13] An electrical insulating composite material comprising a synthetic resin or synthetic rubber composition containing the electrical insulating vapor grown carbon fiber claimed in any one of claims 3 to 5.

[Claim 14] A heat-releasing material comprising the electrical insulating vapor grown carbon fiber claimed in any one of claims 1 to 5.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a vapor grown carbon

fiber coated with boron nitride suitable as an electrical insulating heat-conductive filler, which is used for composite materials comprising a heat-conductive material having high heat conductivity and high electrical insulating property and a composition such as synthetic resin or synthetic rubber, and also relates to a method for producing the vapor grown carbon fiber.

[0002]

[Background Art]

Carbon fibers (hereinafter simply referred to as "CF") in general have excellent properties such as high strength, high elastic modulus, high electrical conductivity and high heat conductivity, and this fiber is being widely used in various composite materials by making use of these properties. The expected uses thereof are not limited only to the products in the field making use of mechanical properties of CF such as high strength and high elastic modulus but include applications to a filler for releasing heat from electronic instruments such as personal computer and portable telephone by making use of high heat conductivity of CF or carbon materials so as to overcome the heat generation trouble ascribable to miniaturization, high densification, high performance and the like of these electronic devices or parts, and also include usage, by making use of their high electrical conductivity, as an

electrically conducting resin filler for electromagnetic wave shielding materials, antistatic materials and the like or as a filler for use in the electrostatic coating to resins so as to satisfy the reduction in weight of motor vehicles. Furthermore, by making use of properties as a carbon material, such as chemical stability, heat stability and fine structure, usage as a field emission material such as flat display is expected.

[0003]

CF is conventionally produced as a so-called organic carbon fiber which is produced by heat-treating and thereby carbonizing fibers such as PAN, pitch and cellulose. In the case of using these fibers as a filler for fiber reinforced composite materials, the contact area with the base material is increased to elevate the reinforcing effect, for example, by reducing the fiber diameter or increasing the fiber length.

[0004]

However, the reduction in diameter of the organic fiber as a starting material of CF is limited and can give at best a fiber diameter of from 5 to 10 μm depending on the production method and fine CF having a fiber diameter of 1 μm or less, particularly on the order of 10 to 200 nm, cannot be produced. Even if such fine CF can be produced, the ratio of length to fiber diameter (aspect ratio) is

limited and the production with good profitability cannot be attained. In this way, CF having a small diameter and a large aspect ratio has not been industrially produced, despite the demand therefor.

[0005]

On the other hand, studies on vapor grown carbon fiber were started in the latter half of 1980s, of which production method is utterly different from that of those organic fibers. As for this vapor grown carbon fiber (hereinafter simply referred to as "pyrolytic CF"), it is known that pyrolytic CF having a diameter of 1 μm or less, approximately tens of nm, can be obtained by the vapor phase pyrolysis of a gas such as hydrocarbon in the presence of a metal catalyst.

[0006]

For example, there have been proposed a method of introducing an organic compound as a starting material, such as benzene, into a high-temperature reaction furnace together with an organic transition metal compound catalyst such as ferrocene by using a carrier gas, and producing pyrolytic CF on a substrate (see, JP-A-60-27700 (the term "JP-A" as used herein means an "unexamined published Japanese patent application")), a method of producing pyrolytic CF in the floated state (see, JP-A-60-54998), and a method of growing pyrolytic CF on the wall of a reaction

furnace (see, Japanese Patent No. 2778434). The pyrolytic CF produced by these methods is heat-treated at a high temperature so as to remove the attached pyrolysis products and enhance the crystallinity, and the obtained final vapor grown carbon fiber (hereinafter, this carbon fiber is simply referred to as "VGCF"; pyrolytic CF, VGCF and the like are sometimes collectively called "vapor growth carbon fiber") is used for various applications.

[0007]

By these production methods, vapor grown carbon fiber excellent in electrical conductivity and heat conductivity, assured of a fine diameter size and a large aspect ratio, and suitable for filler materials, can be obtained. At present, VGCF having a diameter of approximately from 10 to 200 nm and an aspect ratio of approximately from 10 to 500 is easily mass-produced and used as an electrically or thermally conducting filler material, for example, in fillers for electrically conducting resin or in additives for a lead storage battery.

[0008]

The vapor grown carbon fiber is characterized by the shape or crystal structure, and this is a fiber having a structure such that carbon hexagonal network crystals are stacked in a cylindrically rolled form like annular rings and an extremely thin hollow part is present in the center

part.

The crystallinity of the vapor grown carbon fiber is easily enhanced by the graphitization as compared with conventional PAN-type CF and pitch-type CF, but due to reduction in the fiber diameter to approximately from 10 to 200 nm, graphite crystal becomes difficult to grow and poor crystallinity results as compared with natural graphite.

In order to enhance the crystallinity of VGCF, the present inventors have previously disclosed a method of adding a boron compound during the graphitization of pyrolytic CF and thereby doping boron into VGCF, so that the growth of graphite crystal can be promoted and VGCF improved in the crystallinity can be obtained.

[0009]

For improving the heat-releasing property of electronic devices, an electrical insulating material having high heat conductivity is necessary as a heat-releasing filler and for this purpose, alumina and the like are predominantly used. Particularly, accompanying the miniaturization and high densification of electronic devices in recent years, a heat-releasing filler having higher heat conductivity is demanded and to satisfy this requirement, alumina is formed into a spherical shape to improve the filling density in a composite material and thereby elevate the heat conductivity, or aluminum nitride

and the like having higher heat conductivity are used as a heat-releasing filler. The heat-releasing member of an electric device must be electrically insulating in many cases, and the heat-releasing filler is also demanded to be an electrically insulating and highly heat-conductive heat-releasing filler.

[0010]

At present, in the case where electrical insulating property is necessary, fine particles of an inorganic material such as alumina and aluminum nitride are used as the heat-releasing filler, though the heat conductivity is slightly dissatisfied. The heat release is attained by the heat conduction passing through the contact points between fine particles of the filler and thus, the contact point is the rate-determination for the amount of heat released and stands as an obstacle to the heat conduction. On the other hand, since the filler is a fine particle, the contact area for the heat conduction is small and the number of contact points where the heat conduction passes through is large, as a result, the heat releasing property is greatly reduced. Accordingly, for improving the heat release, it is preferred to reduce the number of contact points, for example, to use a thin fibrous heat-releasing filler.

[0011]

[Problem to be solved by the Invention]

An object of the present invention is to provide a vapor grown carbon fiber coated with a fine fibrous electrically insulating material (hereinafter referred to as "coated VGCF"), as a heat-releasing filler for heat-conductive and heat insulating composite materials used in electronic devices, electronic components and the like. The object of the present invention includes providing a method for producing the vapor grown carbon fiber.

[0012]

[Means to Solve the Problem]

The present inventors have succeeded in developing a coated VGCF having an extremely small fiber diameter and ensuring excellent heat conductivity as a whole despite possessing electrical insulating property, by heat-treating pyrolytic CF to improve the crystallinity and thereby enhance the heat conductivity and electrical conductivity and at the same time, coating the surface with an electrically insulating material.

[0013]

More specifically, the above-described object of the present invention have been attained by developing:

[1] an electrical insulating vapor grown carbon fiber comprising a vapor grown carbon fiber having a fiber

diameter of 0.01 to 0.5 μm with a part or the whole of the surface thereof being coated with an electrical insulating material,

[2] the electrical insulating vapor grown carbon fiber as described in [1] above, wherein the electrical insulating material is boron nitride,

[3] the electrical insulating vapor grown carbon fiber as described in [2] above, wherein the boron nitride content is 2% by mass or more based on the entire amount of vapor grown carbon fiber and the Co value is 0.680 nm or less,

[4] the electrical insulating vapor grown carbon fiber as described in [2] or [3] above, wherein the boron content in the depth of 1 nm from the surface of vapor grown carbon fiber is 10% by mass or more,

[5] the electrical insulating vapor grown carbon fiber as described in any one of [1] to [4] above, wherein when compressed to a bulk density of 0.8 g/cm³, the specific resistivity is $10^3 \Omega \cdot \text{cm}$ or more and the heat conductivity is $150 \text{ Wm}^{-1}\text{K}^{-1}$ or more,

[0014]

[6] a method for producing an electrical insulating vapor grown carbon fiber, comprising mixing a boron compound with a vapor grown carbon fiber having a fiber diameter of 0.01 to 0.5 μm , and heat-treating the mixture

at 2,000°C or more in the presence of a nitrogen compound,

[7] a method for producing an electrical insulating vapor grown carbon fiber coated with boron nitride, comprising mixing a boron compound with a vapor grown carbon fiber having a fiber diameter of 0.01 to 0.5 μm , compressing the mixture and heat-treating the compressed mixture at 2,000°C or more in the presence of a nitrogen compound,

[8] the method for producing an electrical insulating vapor grown carbon fiber as described in [6] or [7] above, wherein the nitrogen compound is nitrogen,

[9] the method for producing an electrical insulating vapor grown carbon fiber as described in any one of [6] to [8] above, wherein the boron compound is at least one member selected from the groups consisting of elementary boron, boric acid, borate, boron oxide, B_4C and boron nitride,

[10] the method for producing an electrical insulating vapor grown carbon fiber as described in any one of [6] to [9] above, wherein the mixture of a boron compound and a vapor grown carbon fiber has a boron concentration of 1 to 30% by mass in terms of boron element,

[0015]

[11] an electrical insulating composite material comprising a synthetic resin or synthetic rubber

composition containing an electrical insulating vapor grown carbon fiber comprising a vapor grown carbon fiber having a fiber diameter of 0.01 to 0.5 μm with a part or the whole of the surface being coated with an electrical insulating material,

[12] the electrical insulating composite material as described in [11] above, wherein the electrical insulating material is boron nitride,

[13] an electrical insulating composite material comprising a synthetic resin or synthetic rubber composition containing the electrical insulating vapor grown carbon fiber described in any one of [3] to [5] above, and

[14] a heat-releasing material comprising the electrical insulating vapor grown carbon fiber described in any one of [1] to [5] above.

[0016]

[Mode for Carrying out the Invention]

The present invention is described in detail below.

(Vapor Grown Carbon Fiber)

The CF for use in the present invention is produced by introducing an organic compound (e.g., benzene) as a starting material into a high-temperature reaction furnace together with an organic transition metal compound (e.g., ferrocene) as a catalyst with use of a carrier gas, and

vapor-phase pyrolyzing the organic compound. The fiber diameter thereof is from 0.01 to 0.5 μm and the aspect ratio is approximately from 10 to 500.

Examples of this production method include a method of producing pyrolytic CF on a substrate (see, JP-A-60-27700), a method of producing pyrolytic CF in the floated state (see, JP-A-60-54998), and a method of growing pyrolytic CF on the wall of a reaction furnace (see, Japanese Patent No. 2778434). The CF for use in the present invention may be produced by these methods.

[0017]

The thus-produced pyrolytic CF may be used as it is as a stock material for the coating of an electrical insulating material but at this stage, pyrolysis products derived from the starting material organic compound or the like are adhering to the surface, or the crystallinity of the fiber structure forming the CF is insufficient. Therefore, in order to remove the impurities such as pyrolysis products or enhance the crystal structure as CF, the pyrolytic CF is usually heat-treated in an inert gas atmosphere and used as the stock material.

For the treatment of impurities such as pyrolysis products originated in the starting material, the heat treatment is performed at about 800 to about 1,500°C in an inert gas such as argon. For the improvement of

crystallinity of the carbon structure, the heat treatment is performed at approximately from 2,000 to 3,000°C in an inert gas such as argon. These are commercially available as VGCF.

[0018]

As for the electrical insulating material, organic or inorganic compounds or compositions such as rubber, plastic and glass are known, but in view of resistance against heat or chemicals, inorganic compounds or compositions are preferred and the compound can be used in the form of a melt, a sintered body, a film or the like.

The volume resistivity (Ωcm) of the electrical insulating material may be sufficient if it is 10^{12} or more, preferably 10^{15} or more, and examples of the electrical insulating material which can be used include alumina, sapphire, mica, silica, silicon carbide, aluminum nitride, boron nitride, silicon nitride, sialon, magnesium oxide, beryllium oxide and zirconium oxide. Among these, preferred are boron nitride, silicon nitride and silicon carbide, more preferred is boron nitride.

[0019]

As for the method of coating at least a part of the VGCF surface with an electrical insulating material, the coating, deposition or dipping of an electrical insulating material on VGCF may be employed. In particular, for

coating the VGCF surface with boron nitride of the present invention, a method of mixing a boron compound as a boron source with a vapor grown carbon fiber and heat-treating the mixture with a nitrogen compound working out to a nitrogen source, for example, N_2 , NH_3 , urea, N_2H_4 or a compound of generating N_2 upon reaction, such as NH_3/NO and NH_3/NO_2 , at approximately 2,000 to 3,000°C in an atmosphere containing nitrogen gas (N_2), preferably in an atmosphere of nitrogen gas alone, is preferred. The purity of N_2 may be about 98% or more but is preferably 99.8% or more, more preferably 99.99% or more. The coating conditions may be either a closed system or an open system in an N_2 stream as long as the necessary N_2 concentration can be maintained. The boron compound used here not only serves as a source of boron nitride coated on the VGCF surface but also functions to improve the carbon crystallinity of VGCF.

[0020]

As for the boron compound working out to the boron source, almost all compounds containing boron can be used. This compound is preferably a compound capable of reacting with nitrogen gas in the atmosphere under the conditions of 2,000°C or more to produce boron nitride on the CF surface. Examples of such a compound include elementary boron, boric acid, borate, boron oxide, B_4C and BN. Among these, B_4C and boron oxide are preferred.

[0021]

As for the amount of the boron compound used, the boron concentration in the mixture of boron compound and vapor grown carbon fiber is, in terms of boron element, preferably from 1 to 30% by mass or more, more preferably from 2 to 25% by mass, still more preferably from 5 to 20% by mass. If the boron concentration is less than 1% by mass, the coverage on the VGCF surface is insufficient because of small-amount production of boron nitride and a sufficiently high electric insulating property cannot be obtained, though the crystallinity of VGCF is improved. On the other hand, if the boron concentration exceeds 30% by mass, not only the boron nitride covers the VGCF surface but also boron nitride particles are produced on the fiber surface to reduce the functionality as a fiber.

[0022]

As for the stock material fine fiber, a fiber obtained by previously grinding or powdering the starting material vapor grown carbon fiber may be used. The degree of grinding or powdering may be sufficient if the fiber can be mixed with boron or a boron compound. More specifically, the fiber is further subjected to a filler-forming treatment such as grinding, powdering or classification after the coating treatment with an insulating material (sometimes referred to as "BN coating treatment") and

therefore, the fiber length before the BN coating treatment may not be a proper length suitable for uses but may be sufficient if the carbon fiber can be mixed with boron or a boron compound. The CF obtained by the vapor growth process generally has a size (diameter) of approximately from 0.01 to 1 μm and a length of approximately from 0.5 to 400 μm and can be used as it is. Also, a particle agglomerate (which can be regarded as an independent particle) resulting from aggregation of flocks of the fiber may also be used.

[0023]

The starting material fine vapor grown carbon fiber has a three-dimensional steric structure and not only readily forms a flock state but also has extremely small bulk density and very large void percentage. Moreover, the difference in specific gravity from the boron compound added is large. Therefore, it is difficult to uniformly contact these carbon fiber and boron compound by the mere mixing of these two members.

In order to effectively perform the introduction and reaction of boron, the fiber and boron or a boron compound are thoroughly mixed to attain uniform contact as much as possible. For this purpose, the boron compound particles used must have a particle size as small as possible. If the particle size is large, a high concentration region is

partially generated and gives rise to consolidation. To speak specifically, the particle size is, in terms of the average particle diameter, 100 μm or less, preferably 50 μm or less, more preferably 20 μm or less.

[0024]

In the case of a water-soluble boron compound such as boric acid, a method of adding this compound in the form of an aqueous solution to CF and evaporating the water, or a method of evaporating the water in the heating process, may be used. By uniformly mixing the aqueous solution, the boron compound can be uniformly attached to the fiber surface after the evaporation of water.

[0025]

As described above, the vapor grown carbon fiber has a small bulk density of about 0.01 g/cm³ or less when it is in an agglomerate state after the production. Even in the case of a normal product obtained by heat-treating and then grinding, powdering or classifying this carbon fiber, the bulk density is approximately from 0.01 to 0.08 g/cm³. In this way, such a fine carbon fiber has a large void percentage and if this carbon fiber is subjected as it is to a boron nitride-coating treatment, a heat-treating furnace having a very large volume is necessary and this gives rise to not only high equipment cost but also bad productivity.

Therefore, unlike usual carbon materials, the boron nitride-coating treatment must be performed in a higher efficiency manner.

[0026]

For example, after uniformly mixing the fiber and boron or a boron compound, the mixture as it is may be heat-treated, however, the mixture is preferably highly densified and while maintaining (fixing) this state as much as possible, heat-treated. For realizing this, a method of mixing the fiber and boron or a boron compound and then fixing the mixture through pressurization, compression and high densification before the heat treatment is preferably used in the present invention.

In this case, the fiber and boron or a boron compound may be mixed by any mixed insofar as the uniformity can be maintained. The mixing apparatus may be any commercially available mixing apparatus if uniform mixing can be attained, but fine carbon fibers readily flock and therefore, a Henschel mixer type with a chopper for grinding the flocked carbon fibers is preferred. The stock fiber used may be the produced fiber itself as described above or may be a product obtained by heat-treating the fiber at a temperature of 1,500°C or less. However, in view of the profitability and the performance, a method of mixing the produced fiber itself is preferred.

[0027]

As for the method of highly densifying and fixing the mixture of fiber and boron or a boron compound not to cause separation between the fiber and the boron or boron compound, any method may be used, such as a forming method, a granulation method or a method of compressing and stuffing the mixture into a fixed shape in a crucible or the like. In the case of a forming method, the formed article may have any shape such as columnar, plate-like or rectangular.

[0028]

The bulk density of the highly densified and fixed mixture is 0.02 g/cm^3 or more, preferably 0.03 g/cm^3 or more.

When the pressure is released after compressing the mixture into a formed article, the volume is somewhat expanded to lower the bulk density. In this case, the bulk density at the compression is adjusted to give a bulk density of 0.02 g/cm^3 or more when fixed after the release of pressure. For elevating the treatment efficiency, the fiber charged into a vessel may also be compressed or heat-treated in the compressed state by using a pressure plate or the like to give a bulk density of 0.02 g/cm^3 or more.

[0029]

After the addition of a boron compound and subsequent densification, the fiber is heat-treated.

The heat-treatment temperature for coating the VGCF surface with boron nitride must be from 2,000 to 3,000°C, preferably from 2,000 to 2,500°C. If the treatment temperature is less than this range, boron nitride is not produced and the graphite crystal of VGCF grows insufficiently.

[0030]

In the heat treatment, a normal graphitization furnace such as resistance heating furnace, high frequency furnace and Acheson furnace can be used. During the elevation of temperature up to the heat-treatment temperature, production and diffusion of boron occur due to decomposition of the boron compound. Therefore, the temperature elevation time is preferably shorter. For facilitating the diffusion of boron, it may be also possible to place a mixture of a boron compound and VGCF in a vessel such as graphite crucible, and heat-treat the mixture.

The vapor grown carbon fiber before the heat treatment with a boron compound may be any one of the pyrolytic CF itself before the heat treatment for removing pyrolysis products such as tar adhering to the surface of the fiber after the production, a fiber obtained by heat-treating the pyrolytic CF in an inert gas such as argon at about 800 to about 1,500°C, and VGCF after graphitization at

about 2,000 to about 3,000°C for enhancing the crystallinity of the carbon structure.

[0031]

The nitrogen atmosphere at the heat treatment may be sufficient insofar as, for example, in the case of a high frequency heating furnace using a graphite cylinder as a heat generator, the nitrogen atmosphere can be maintained.

In the present invention, the "coating" may be sufficient if boron nitride is present on at least a part of the VGCF surface. The boron nitride preferably occupies 70% or more, more preferably 80% or more, of the entire surface and may be present evenly or unevenly. The density may be high or low, however, the boron nitride is preferably present entirely rather than partially. In the depth of about 1 nm from the surface, the surface boron content as determined by the X-ray photoelectron analysis is 10% by mass or more, preferably 20% by mass or more, more preferably 30% by mass or more. The boron content of the entire VGCF may be 2% by mass or more. Also, B or N may be present not only on the VGCF surface but also in the inside of VGCF.

[0032]

The electrical insulating property of the boron nitride-coated VGCF of the present invention can be evaluated by the resistivity thereof. As for the method of

measuring the resistivity, since the coated VGCF is powder, the resistivity of the powder consolidated to a bulk density of 0.8 g/cm^3 is measured. The resistivity of the coated VGCF of the present invention is $10^3 \Omega \cdot \text{cm}$ or more, preferably $10^5 \Omega \cdot \text{cm}$ or more, more preferably $10^6 \Omega \cdot \text{cm}$ or more. The heat conductivity of the boron nitride-coated VGCF of the present invention is greatly affected by impurities or porosity but is preferably $150 \text{ Wm}^{-1}\text{K}^{-1}$ ($150 \text{ Jm}^{-1}\text{s}^{-1}\text{K}^{-1}$) or more at room temperature.

[0033]

The VGCF of the present invention is a carbon fiber enhanced in the crystallinity, and the boron nitride coated has good heat conductivity. However, the heat conductivity of VGCF is governed by its crystallinity and therefore, the heat conductivity can be evaluated by C_o as an index for the graphite structure of carbon. The C_o value is preferably 0.680 nm or less. If the C_o exceeds this range, good heat conductivity cannot be obtained. In the case of incorporating the carbon fiber of the present invention into a synthetic resin to obtain an electrical insulating composite material, the synthetic resin may be plastic, synthetic rubber or the like. In the case of using the boron nitride-coated VGCF of the present invention as a heat-releasing filler for plastic or the like, the heat conductivity of the material varies depending on the VGCF

content, but the heat conductivity of the material can be measured by a plate comparison method according to JIS A-1412, a cylinder method, a plate direct method or a non-stationary method such as laser flash method.

According to the present invention, a coated VGCF having good heat conductivity and high electrical insulating property can be provided, and this carbon fiber can be very advantageously used as a heat-releasing filler of composite materials, such as radiation board of electronic devices and the like.

[0034]

[Examples]

The present invention is described in detail below.

(Example 1)

A pyrolytic CF having a fiber diameter of 0.1 to 0.2 μm and an aspect ratio of about 20 to about 500 was produced by the method described in Japanese Patent No. 2,778,434. This pyrolytic CF was stuffed into a graphite crucible and heat-treated at 1,200°C for 20 minutes in an argon atmosphere.

The heat-treated CF was taken out and mixed with 10% by mass of B_4C (produced by Wako Pure Chemical Industries, Ltd.). The mixture was again stuffed into a graphite crucible and heat-treated in a nitrogen atmosphere by elevating the temperature to 2,400°C over about 2 hours and

keeping the temperature for 60 minutes in this Example as a holding time necessary for homogenizing the temperature to the center of the graphite crucible.

[0035]

After the heat treatment, a classification operation as a post-treatment was performed to remove carbon particles and the like produced as a by-product at the production of coated VGCF, and the obtained carbon fiber was used as a boron nitride-coated VGCF sample.

This sample was evaluated by measuring the boron content based on the VGCF total amount, the resistivity and the Co value. The results obtained are shown in Table 1. Furthermore, the contents of boron and nitrogen on the surface of the vapor grown carbon fiber coated with boron nitride of the present were determined by the X-ray photoelectron analysis, as a result, the boron content and the nitrogen content in the depth of about 1 nm from the surface were such that boron was 39% by mass and nitrogen was 50% by mass.

[0036]

(Example 2)

The same treatment as in Example 1 was performed by changing the amount added of B_4C to 20% by mass. The evaluation results thereof are shown in Table 1.

[0037]

(Comparative Example 1)

The same treatment as in Example 1 was performed by not adding B₄C. The evaluation results thereof are shown in Table 1.

(Comparative Example 2)

The same treatment as in Example 1 was performed in an argon atmosphere in place of the nitrogen atmosphere. The results obtained are shown in Table 1.

[0038]

[Table 1]

Evaluation Item	Boron Content (% by mass)	Co (nm)	Resistivity ($\Omega \cdot \text{cm}$)
Example 1	4	0.677	1×10^4
Example 2	8	0.675	1×10^5
Comparative Example 1	<0.05	0.683	0.01
Comparative Example 2	4	0.677	0.005

[0039]

(Example 3)

A composite material with PET containing 30% by mass of the boron nitride-coated VGCF obtained in Example 1 was prepared, and the heat conductivity was measured by the laser flash method.

The heat conductivity was $45 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature in the orientation direction of the boron nitride-coated VGCF.

[0040]

[Effects of the Invention]

According to the present invention, an electrical insulating VGCF having good heat conductivity can be provided, and this fiber can be used particularly as a heat-releasing filler of composite materials, such as radiation board of electronic devices.

In particular, the surface of VGCF having a fiber diameter of 0.01 to 0.5 μm is coated with boron nitride, whereby the resistivity of the fiber when compressed to a bulk density of 0.8 g/cm^3 becomes $10^3 \Omega \cdot \text{cm}$ or more.

Furthermore, the fiber exhibits a heat conductivity of $150 \text{ Wm}^{-1}\text{K}^{-1}$ or more at room temperature and thus, can have high heat conductivity.

[NAME OF THE DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a vapor grown carbon fiber coated with a fine fibrous electrically insulating material, as a heat-releasing filler for heat-conductive and heat insulating composite materials used in electronic devices, electronic components and the like; and a production method thereof.

[MEANS TO SOLVE THE PROBLEM]

An electrical insulating vapor grown carbon fiber comprising a vapor grown carbon fiber having a fiber diameter of 0.01 to 0.5 μm with the surface thereof being coated with an electrical insulating material which is boron nitride, wherein when compressed to a bulk density of 0.8 g/cm^3 , the resistivity is $10^3 \Omega \cdot \text{cm}$ or more and the heat conductivity is $150 \text{ Wm}^{-1}\text{K}^{-1}$ or more; and a method for producing an electrical insulating vapor grown carbon fiber coated with boron nitride, comprising mixing a boron compound with a vapor grown carbon fiber having a fiber diameter of 0.01 to 0.5 μm , and heat-treating the mixture at 2,000°C or more in the presence of a nitrogen compound.